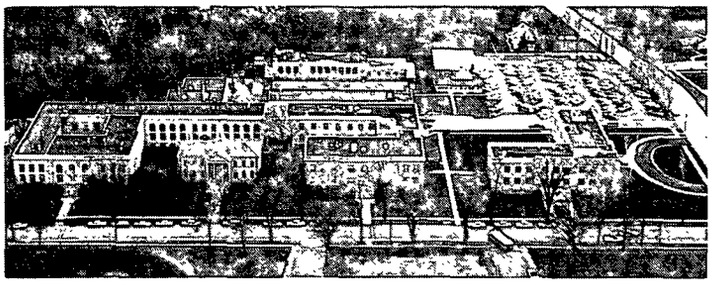

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THE OZONE OXIDATION OF ALKALI–FIBERIZED LOBLOLLY PINE WOOD

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ABSTRACT

Gas phase ozonations of alkali-fiberized loblolly pine (FW) to 1, 3, 5, and 7% consumption levels were run at 45% consistency and 10°C in a tumbling reactor. The pulps were compared with controls using conventional analytical methods and FT-IR difference spectroscopy. These techniques indicated in situ lignin was slightly oxidized, had more carboxyl and unconjugated carbonyl, and less phenolic hydroxyl groups than the unoxidized control. The methoxyl content of the residual ozonated lignin was not greatly affected by the treatments. The water-soluble oxidation products were derived principally from lignin. Small amounts of carbohydrate were dissolved but there was little evidence of severe carbohydrate degradation of the oxidized pulps. A comparison of conventional and FT-IR techniques for the detection of functional groups in lignin showed qualitative agreement for carboxyl analyses. Uncertainties render carbonyl analyses by FT-IR difficult. A discrepancy was noted between methylation and FT-IR techniques for the detection of phenolic hydroxyl.

Introduction

Ozone has potential for use in pulping and bleaching as well as in offering a unique solution to some environmental problems faced by the pulp and paper industry. The chemistry of ozonation is complex (1,2) and its behavior during pulping is not clearly understood. The objective of this research is to elucidate the manner in which the lignin and carbohydrate components of loblolly pine fiberized wood (FW) is modified by ozone treatment.

Experimental

FW was prepared at the Bauer Brothers thermomechanical pilot plant in Springfield, Illinois by a process recommended by Nichols, et al. (3). Wood chips were pretreated with a sodium carbonate solution (Na_2CO_3 40.7% o.d. wood) at 10% consistency for 30 minutes at 92°C. After draining, the carbonate-impregnated chips (40% consistency) were fiberized in a No. 418 Bauer double disk (0.030-inch disk clearance) pressurized refiner at 160°C, 80 psig steam pressure for 6 minutes. Extractives were removed by Soxhlet extraction using 9:1 acetone:water. Washing with hot (78°C) deionized water completed the purification process.

Ozone from a Welsbach Laboratory ozonator, Model T-816 (calibrated to determine the rate of ozone production) was led into a 5 liter round bottom reaction flask containing FW attached to a Buchi Model R evaporator. The exit gases flowed through two 500 mL gas washing bottles filled with KI solution. FW in the flask (60 g) was reacted at 10°C, pH 6.6 at a flow rate of 3 L/min for 3.7, 11, 18.6, and 25.6 minutes (to give ozone consumptions of 1, 3, 5, 7% of o.d. FW) at efficiencies decreasing linearly from 99 to 94% of applied ozone. Analyses were conducted on unwashed ozonated FW, hot water-washed (78°C) ozonated FW as well as appropriate controls.

The pulps were analyzed for Klason lignin (4) and soluble lignin (5), methoxyl (6), carboxyl (7), holocellulose content (8), viscosity (9), carbohydrate content (10) and phenolic hydroxyl (11) by conventional techniques.

Infrared spectra were obtained from transmittance measurements made on KCl pellets containing finely powdered anhydrous FW using a Nicolet 7199 Fourier Transform infrared spectrometer. The measurements, taken at 200 scans per sample with 2 wave number resolutions, were recorded as percent transmittance vs. wave number and stored in the memory of the spectrophotometer. The difference spectra of interest were obtained by balancing the individual spectra in the C-H region (2900 cm^{-1}). After converting to absorbance, the reference spectra were multiplied by the appropriate weighting factor and subtracted to give the desired difference spectrum.

Results and discussion

The loblolly pine fiberized wood (FW) employed in this investigation was prepared by a technique which ensured a greater separation of fibers in the middle lamella region than is the case when fiberization is carried out at lower temperature (3). In this way, lignin rather than carbohydrate would be exposed initially to the action of ozone.

The production and consumption of ozone was linear with time of reaction. The crude yield of pulp was greater than 100%. After the removal of the water soluble components, yield decreased linearly with ozone consumption (Table I). The selectivity of ozone for lignin may be seen at 7% ozone consumption where 39% of the lignin was removed in contrast to only 5% of the carbohydrate. The significant lignin losses at higher levels of ozone application (5% or greater) suggest it may be a pulping agent (albeit expensive) under these conditions. This behavior is probably due to the preferential electrophylic attack on the abundant and accessible

aromatic and olefinic units of lignin. However, we cannot rule out selectivity due to greater accessibility of lignin in the fiberized wood.

The methoxyl content of the pulp decreased linearly with ozone application but the methoxyl content of the remaining lignin in the pulp remained relatively constant (approximately 16.3%) regardless of ozone consumption (Table I). It was concluded that the loss of methoxyl occurred during or after the loss of lignin.

The lignin-free yields of ozonated, washed FW indicate carbohydrate solubilization as a result of these reactions is minimal (Table I). Since most of the arabinogalactan and other highly soluble polymers of pine would have been removed by hot aqueous treatments during fiberization (12,13), the polysaccharide content of FW was calculated from hydrolysis data in terms of 4-O-methylglucuronoarabinoxylan, galactoglucomannan, and cellulose contents. The data in Table II indicate that 17% of the "xylan" and 8% of the "mannan" was removed after reaction with 7% ozone. The cuene viscosities of the pulps indicate a slight increase in molecular weight as a result of ozone treatments which probably reflects the loss of the low molecular weight hemicelluloses (14) and suggests that cellulose degradation was not extensive.

The infrared transmission spectra of the chlorite holocelluloses prepared from FW and ozonated FW were identical. This observation combined with the above data suggests that carbohydrate effects (with one exception to be mentioned later) would not contribute greatly to the interpretation of FT-IR difference spectra.

A comparison of the nature of the functional groups in FW before and after reaction and after extraction with hot (78°C) water can give a picture of chemical changes wrought by ozone. The carboxyl contents of untreated and ozonated FW were estimated using the conventional TAPPI procedure (see Table III). Leopold (15) found

20 meq/100 g o.d. wood for untreated loblolly pine while Soteland (16,17) found 7 meq/100 g o.d. for a TMP pine pulp. The carboxyl content of 12.6 meq/100 g o.d. obtained here is consistent with Soteland's observation that acidic substances are removed from pine as a result of TMP treatments.

The carboxyl contents of the pulps increased after ozonation but remained relatively constant with increasing levels of oxidation as shown in Table III. This increase in carboxyl content cannot be attributed specifically to any component of wood. The FT-IR spectra of holocelluloses derived from these FW products cannot be subtracted from the total spectra because the chloriting process introduces carboxyl groups into them. It is speculated, however, that most of the carboxyl formation involves lignin because at least 75% of the soluble products are derived from lignin.

Since the extinction coefficients of the functional groups in their different environments are not known, only a qualitative estimation of the changes can be made when the IR spectra of the FW samples are compared. If it is assumed that the wavelength of absorbance and the extinction coefficients remain relatively constant, although unknown, between samples, semiquantitative estimation of chemical changes can be made analogous to the difference technique described by Vander Linden (19). For example, in the FT-IR spectrum of an acidified wood sample, all carboxyl appears as the acid and absorbs in the infrared at 1725 cm^{-1} along with the absorption due to unconjugated carbonyl. In a neutralized wood spectrum, all carboxyl appears as the anion and absorbs at about 1605 cm^{-1}. The difference spectrum between these two results was obtained by subtracting the acidified FW spectrum (after balancing on the IR spectrophotometer and conversion to absorbance) from the neutralized FW spectrum (Fig. 1). Examples of such spectra are shown in Fig. 1. The IR absorbances shown in Table III parallel the carboxyl contents measured by the TAPPI

procedure. The major deviation after 5% ozone consumption may represent an error in the TAPPI estimation rather than an inconsistency in the FT-IR technique.

Potentiometric titration of the water-soluble fractions showed linearly increasing amounts of water soluble carboxyl were produced with increasing ozone application (Table III). The IR spectra of the soluble components after 5 and 7% ozone application showed evidence for the presence of carboxylic acids. An intense band was seen at 1720 cm^{-1} which was attributed to the carbonyl stretching mode in saturated aliphatic acids (19,20). A broad and intense band at 3300 to 3500 cm^{-1} was also present which is thought to be the O-H stretching vibration of hydroxyl groups in carboxylic acids (19,20). Qualitative GLC analysis of the isolated water-soluble components showed a large number of small responses corresponding to low molecular weight acids such as glyceric, glyoxalic, as well as oxalic acid which itself amounted to 10% of the extract (21).

FT-IR difference spectroscopy was employed to detect carbonyl in untreated and ozonated FW. By making the assumptions mentioned earlier, differences in carbonyl can be crudely estimated. The types of difference spectra and the information provided is as follows: Total carbonyl produced by ozonation can be detected by subtracting the untreated FW spectrum from the ozonized, unwashed FW spectrum. Carbonyl in the insoluble FW can be obtained by subtracting the untreated FW spectrum from the ozonized, washed FW spectrum. Water-soluble carbonyl can be observed by subtracting the ozonized washed FW spectrum from the ozonized unwashed spectrum, while noncarboxyl carbonyl in ozonated FW can be detected by subtracting the untreated, neutralized FW spectrum from the ozonized, washed neutralized FW spectrum.

The infrared absorbance at 1725-1730 cm^{-1} in FW spectra is representative of the C=O stretching mode of unconjugated carbonyl groups (19,20). The positive values of the absorbances shown in Table IV suggest carbonyl is formed during the oxidation and that greater levels of ozonation result in greater carbonyl formation. The total insoluble unconjugated carbonyl represents the spectra of both true carbonyl and carboxyl-carbonyl. These may be differentiated from one another by infrared measurements on neutralized FW samples in which the carboxyl component of the absorbance is shifted to 1605 cm^{-1}. Table III gives the absorbance values for unconjugated, insoluble, noncarboxyl carbonyl and the total insoluble unconjugated carbonyl. A direct comparison between the noncarboxyl carbonyl and the total carbonyl absorbance cannot be made. Since the carboxyl content of the insoluble ozonated FW remained constant, the increase in carbonyl content observed here must be due to changes in noncarboxyl carbonyl.

The conjugated carbonyl groups in the FT-IR difference spectra of FW were represented by absorbance at approximately 1660 cm^{-1} [the characteristic C=O stretching vibration of conjugated carbonyl (19,20)]. This absorbance is associated only with lignin. Hergert (22) suggested the 1660 cm^{-1} absorbance was attributable to a ketone alpha to an aromatic ring with the para position etherified and an oxygen on the beta position.

The conjugated carbonyl contents of untreated and ozonated FW are shown in Table III. Positive absorbance values, found for total carbonyl content at higher ozonation levels of treatment, suggest oxidative formation of those groups. The extent of conjugated carbonyl formation remained relatively constant regardless of the level of ozone application.

The negative absorbance values found for the insoluble conjugated carbonyl suggests less of those groups in ozonated FW than in untreated FW. Thus it can be

speculated that the oxidation of wood (probably lignin) with ozone results in the formation of conjugated carbonyl groups. These groups are associated with the severely degraded fractions of wood and are readily removed by water extraction. Several mechanisms for the production of conjugated carbonyl groups in lignin are possible. These include 1,3 dipolar addition of ozone to aromatic rings [proposed by Soteland (23)], electrophilic substitution of ozone at aromatic rings leading to demethoxylation and quinone formation (24), ozone insertion at an alpha carbon to form a conjugated alpha carbonyl group and possibly degradation by way of a Criegee mechanism (25) to form a conjugated aldehyde.

The phenolic hydroxyl content of untreated and ozonated FW was estimated by a selective methylation technique similar to that developed by Andrews and Des Rosiers (11). The phenolic hydroxyl content of the residual lignin in extracted ozonated FW showed a slight decrease over the control. Hergert (22) and Bellamy (19) attribute the absorbance at 1200 to 1220 cm^{-1} to the C-O stretch of the phenolic hydroxyl group. This particular absorbance was absent in the spectrum of holocelluloses. The neutralized FW difference spectra and the untreated FW difference spectrum were used to obtain a normalized spectrum. The phenolic hydroxyl values obtained using this procedure indicate a significant loss of phenolic groups as a result of ozonation. Both methods of phenolic hydroxyl determination are subject to theoretical uncertainties which only future research can resolve.

Conclusions

Ozone reacts with FW by a zero order reaction in which lignin is preferentially removed by a hot water wash. Carbohydrate degradation is minimal. The carboxyl content of the residual FW increases slightly in contrast to the carboxyl-rich soluble fraction. FT-IR analyses indicate the unconjugated carboxyl of residual FW increases greatly and the conjugated carbonyl decreases slightly as a result of these

treatments. The phenolic hydroxyl content decreased. This behavior can be rationalized by known ozone reactions.

The relative agreement between carboxyl by chemical and FT-IR analyses suggests the latter has the potential for a quantitative test. The uncertainty accompanying FT-IR analyses of carbonyl and phenolic hydroxyl must be eliminated before a useful analytical procedure can be developed.

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I. Gas-phase ozonation of alkali-fiberized loblolly pine[a]

Ozone, %	Washed yield, %	Lignin[b] content, %	Solubilized lignin, %	Lignin-free yield, %	Methoxyl of washed pulp, %	Methoxyl[c] of lignin, %
0	100	28.1	0	100	4.85	16.0
1	98.8	26.6	5	100.4	4.58	16.0
3	93.3	22.8	19	98.1	3.91	15.9
5	90.8	19.9	29	98.5	3.64	17.0
7	85.7	17.2	39	95.3	3.30	16.4

[a]All values on acetone-extracted, o.d. fiberized wood basis.
[b]Klason + acid soluble lignin.
[c]Assuming 16.0% MeO in lignin of untreated FW, which represents 93% of total methoxyl content for untreated and ozonated FW.

II. Polysaccharide content of ozonated alkali-fiberized pine pulps[a]

Ozone, %	4-O-Methylglucurono-[b] arabinoxylan, %	Galactogluco-[c] mannan, %	Cellulose,[d] %	Holo-cellulose, %	Viscosity, dL/g
0	7.7	18.0	42.2	100	22.6
3	6.8	17.6	42.2	98.1	24.5
5	--	--	--	--	
7	6.4	16.6	42.2	98.6	26.4

[a]All values on acetone-extracted, o.d. fiberized wood basis.
[b]Calculated to include all arabinose and xylose in hydrolyzate.
[c]Calculated to include all galactose and 1/3 as much glucose as mannose in hydrolyzate.
[d]All glucan not included in c.

III. Carboxyl and carbonyl production as a result of ozonation of pine pulp

Ozone, %	Carboxyl insoluble fraction, meq/100 g	Carboxyl soluble[b] fraction, meq/100 g	Total carboxyl, meq/100 g	Carboxyl absorbance[c] of insoluble fraction at 1650 cm^{-1}	Insoluble[d] unconjugated carbonyl absorbance at 1730 cm^{-1}	Insoluble[d] conjugated carbonyl absorbance at 1660 cm^{-1}
1	3.0	5.0	8.0	0.063	0.022	-0.004
3	2.9	41.2	44.1	0.062	0.039	-0.013
5	3.8	77.6	88.4	0.062	0.051	-0.004
7	3.3	102.6	105.9	0.067	0.067	-0.011

[a]Based on TAPPI Standard T-237.
[b]Carboxyl content of wash filtrate determined by potentiometric titration.
[c]Based on FT-IR difference spectra of neutralized FW minus acidified FW.
[d]Based on FT-IR difference spectra of ozonized washed FW minus untreated FW.

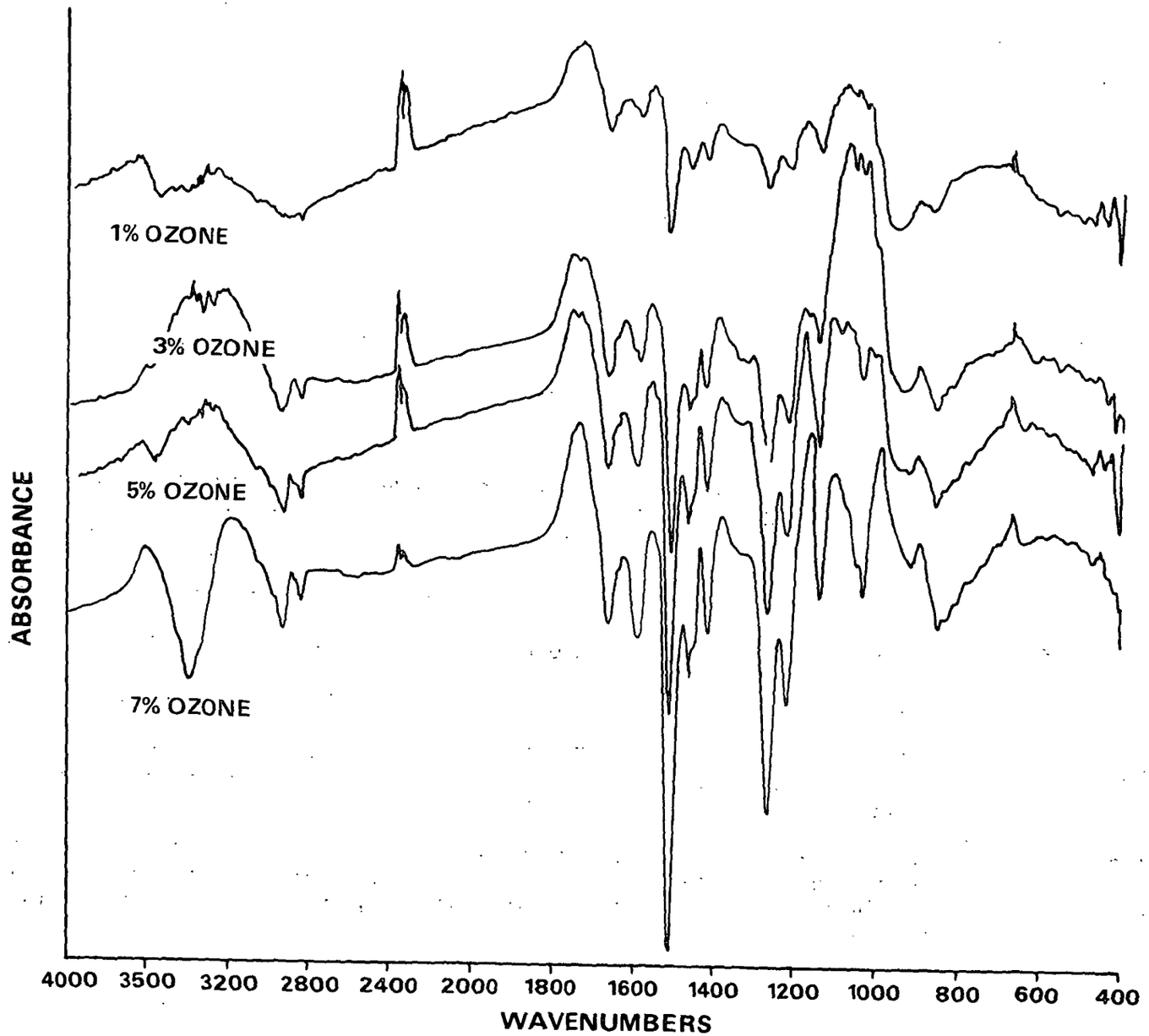

Figure 1. The FT-IR Difference Spectra of 1,3,5 and 7% Ozonized, Washed Neutralized FW minus Untreated Neutralized FW